A

Thesis

On

Separation of Chromium (VI) by Bulk Liquid Membrane Technique

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Submitted by

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In partial fulfilment for the award of the Degree of

***Master of Technology in* Chemical Engineering**

Roll No. 213CH1116

Under the Supervision of

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DEPARTMENT OF CHEMICAL ENGINEERING

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CERTIFICATE

This is to certify that **Mr. Snehasis Biswas** has carried out the project work entitled "***Separation of Chromium (VI) by Bulk Liquid Membrane Technique***" within the stipulated time. It is hereby approved that the work done by him is a creditable study in the field of chemical engineering and is carried out with all the details and precisions for the fulfilment of the purpose under my supervision and guidance.

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In pursuit of this academic endeavour, I feel that I have been singularly fortunate; inspiration, guidance, direction, co-operation, love and care all came in my way in abundance and it seems almost an impossible task to acknowledge the same in adequate terms. Yes, I shall be failing in my duty if I do not record my profound sense of indebtedness and heartfelt gratitude to my guide **Dr. Pradip Chowdhury** who guided me in pursuance of this work. His association will remain a beacon light to me throughout my career.

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ABSTRACT

In this work an attempt has been made for faster extraction and separation of Cr (VI) from its model solution with minimal use of carrier. Studying the effects of various process parameters *viz*. source and stripping phase concentration and pH on the overall performance of this bulk liquid membrane technique have been a key objective along with the membrane reusability. Aqueous solution of potassium dichromate ($K_2Cr_2O_7$) was used as the source phase or model contaminant for Cr (VI) ions. 1, 2-dichloroethane was the preferred solvent used as the liquid membrane phase in this work. Aqueous solution of NaOH was found to be the effective stripping phase. Performances of several carriers had been investigated and *tri-n-octylamine* (TOA) was found to be the most suitable in facilitating the transport mechanism. A comprehensive kinetic study was carried out and the effect of various parameters *viz*. carrier concentration, feed and stripping phase concentrations and pH were studied. A key objective of this work was to achieve maximum separation of Cr (VI) with minimal carrier concentration and this work successfully reports a removal percentage of *ca*. 98% of Cr (VI) ions with 0.25 vol. % of TOA within a span of 2 hrs. The transport mechanism was observed to be more effective in the acidic pH range *w.r.t* the feed phase (*ca*. pH 1) whereas the optimum stripping phase concentration of NaOH was 0.3 N. Membrane reproducibility study showed that the performance of the liquid membrane remained largely unaffected even after fourfold use.

CONTENT

LIST OF ABBREVIATIONS

BLM	Bulk Liquid Membrane
DOA	*dioctylamine*
DTPA	*diethylene triaminepentaacetic acid*
ELM	Emulsion liquid membrane
HFSLM	Hollow fibre supported liquid membrane
ppm	Parts per million
RPM	Rotation per Minute
SLM	Supported Liquid Membrane
TIOA	tri-isooctylamine
TOA	*tri-n-octylamine*
TOMAC	*tri-n-octylmethylammonium chloride*
WHO	World Health Organization

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CHAPTER 1

INTRODUCTION

In this chapter the background and motivation behind researching this area has been elucidated. The key research objectives are properly narrated.

1.1. Background of Present Research Work

Heavy metal contamination in water bodies is a major source of pollution and it requires urgent attention before it reaches catastrophic proportions. Chromium is a well-known heavy metal borne out of various processes predominantly from leather tanning, textile, metallurgical, pulp-paper and pigment industries [1] and once they remain untreated, the effluent contaminates large swathe of fresh water bodies, causing widespread pollution. Although chromium is found in different ionic forms or oxidation states, the trivalent and hexavalent forms i.e. +3 and +6 are of more common occurrence [2], albeit there are unstable oxidation states like +1, +4 and +5 exists as well. Cr (VI) is reportedly more toxic, mobile and carcinogenic (due to its mobility to move across biological cells) than its reduced form i.e. Cr (III) [3-4]. World Health Organization (WHO) guidelines limit the maximum chromium concentration to be less than 0.05 ppm in potable water [5]. Several methodologies have been proposed upon careful investigation by various researchers on removal of hexavalent chromium from industrial wastewater. A careful review of literature shows liquid-liquid extraction [6, 7], ion exchange [8], reverse osmosis [9], adsorption [10] and membrane based separation techniques [11] to be some of the effective routes from an extensive list.

Liquid membrane processes are in vogue and is fast emerging to be one of the most sought after techniques in separation applications. Some of their key features include: low cost, simple operability, high selectivity, and energy efficient and importantly, combining both extraction and stripping in a single unit operation. There have been several reports on separation of Cr (VI) using different liquid membrane techniques *viz*. bulk liquid membrane (BLM) [12], supported liquid membrane (SLM) [13] and emulsion liquid membrane (ELM) [14]. The effectiveness of various carriers *viz*. *aliquat 336* [15], *tri-n-octylamine* [16], *tri-n-dodecylamine*, *tri-n-butylphosphate* [17], *p-tert-butylcalix[4]-arenedioxaoctylamide derivative* [18] on the transport mechanism of Cr(VI) in liquid membrane setup have also been investigated by various researchers.

Although the performances of ELM and SLM show faster separation kinetics, however, membrane stability has always remained a concern. Because of its simplicity in design and being inexpensive coupled with better phase stability, BLM technique has been an attractive proposition in this type of separation applications.

1.2. Research objectives

The main objectives of present research work can be summarized as follows:

(a) Separation of hexavalent Chromium by bulk liquid membrane technique

(b) Selecting a suitable amine functionalized carrier from a select group for better performance in terms of minimum use for maximum separation performance

(c) Optimizing the manifold parameters viz. carrier concentration, strip phase concentration, pH of the feed phase during the transport process

(d) Studying the detailed kinetics of the 3-phase transport process in the BLM ensemble

(e) Studying reusability of the liquid membrane for multiple runs

1.3. Thesis Summary

This thesis paper consists of five chapters *viz.* Introduction, Literature Review, Experimental work, Results and Discussion and Conclusions & Future Scope. Individual of these chapters contain details about past and present research work in associated fields, experimental procedure followed, research outcomes and their possible explanations.

Chapter 1: Introduction of the research field in brief, broad details of research background, objectives of this work and thesis overview.

Chapter 2: Discussion of the literature reports in detail pertaining to the field of Liquid Membranes. Various terminologies related to Liquid Membranes especially on Bulk Liquid membrane has been introduced and elaborated.

Chapter 3: Details experimental work including membrane preparation, experimental procedure, concentration analysis, along with schematic diagram

Chapter 4: Incorporates numerous results obtained from these experiments and their possible justification.

Chapter 5: Summarization of the key highlights of this work and concludes the findings along with possible future scope.

CHAPTER 2

LITERATURE REVIEW

In this chapter the basics on working principle of liquid membrane operation are discussed from fundamental point of view. Also, various types of liquid membrane operations are explained with diagrammatic representation.

2.1. Basics on liquid membranes and their classifications

A membrane is a semi permeable barrier between two phases. Separation occurs when transport rate through membrane is different for different component. Membrane is widely used in industries for separation process. As membrane separation is one of the cost efficient method along with its simplicity in operability, making it very useful unit operation process for industrial applications. The basic mechanism of transport process involving liquid membranes is pronged between source and membrane phase, the process is similar to liquid-liquid extraction, whereas, between membrane phase and strip phase, there has been simultaneous recovery occurring. Thus, a liquid membrane set-up effortlessly combines two unit operations within a single unit. It employs an organic solution including a carrier, immiscible with water, flowing or stagnant between two aqueous phases (feed or source and strip phases or receiving phases). In general, the feed and stripping phases are aqueous and the membrane is organic, but the alternative reverse arrangement can also be possible. Liquid membrane comprise of three distinct phases, the feed phase, the membrane phase and the stripping phase. The feed phase is the water, containing the metal ions or the other species (organic waste) to be extracted and the stripping phases is where the metal ion will be trapped. The commonly established mass transfer mechanism for the transport of a solute in liquid membrane is reaction-diffusion. The solute species diffuse to liquid membrane from aqueous feed phase due to a concentration gradient. Solubility and diffusion coefficient of different solutes have different values in a liquid membrane. The selectivity and efficiency of transport across the membrane could be strikingly enhanced by carrier in the organic phase membrane. Carrier is the heart of liquid membrane, which reacts reversibly and rapidly with the preferred targeted solute to form a mixture of feed solution. This process is known as carrier-mediated or facilitated liquid membrane separation.

Liquid membrane, according to their working principle, can be classified broadly into three types [19]. They are:

1) Bulk liquid membrane (BLM)
2) Supported liquid membrane (SLM)
3) Emulsion liquid membranes (ELM)

2.1.1. Bulk Liquid Membranes

Bulk liquid membrane is the simplest form of LM processes. The BLM set up is divided in two compartments: one contains the feed phase and other having the stripping phase, separated by a solid impermeable barrier. A membrane organic phase containing a diluent along with carrier is placed at the top or bottom of the aqueous phases according to their density difference with respect to the aqueous phases. The targeted substance can only transport through liquid membrane with the help of carrier present in LM. The liquid membrane makes contact with the two aqueous phases and affects the solute transfer between them. Organic diluent liquid plays as a mediator only and its extraction capacity does not significantly affect the transport. As a result, a variety of immiscible, harmless and inert organic liquids is suitable as an intermediate diluent liquid, containing only a small amount of carrier.

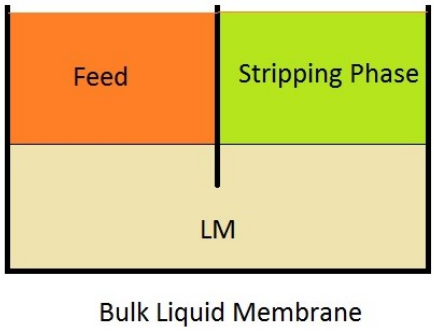

Figure 2.1 Schematic of BLM

A small amount carrier is able to handle large concentration substance efficiently. For fastening mass transfer rate all three liquids are stirred with a favourable speed (rpm). Figure 2.1 shows the structure of BLM systems. In this process extraction and stripping of targeted

substance occurs simultaneously [20]. This amalgamation of two mass transfer operations offers two considerable advantageous over the traditional liquid–liquid extraction.

2.1.2. Supported liquid membrane

A LM is designed by placing a thin layer of supported organic liquid phase between feed phases and strip phase. A microporous polymer or ceramic is used as a support for this liquid membrane, a thin film of organic layer can be immobilized onto the micro-porous support. The polymeric or ceramic support is usually used for providing mechanical support to the liquid membrane. Generally microporous hydrophobic polymers is used for SLM, some ceramic support can also be used. The support does not play an active role in the separation. Different types of configuration of SLM can be used e.g. a flat sheet or a spiral-wound type (for higher surface area) in which it does let the membrane liquid to repose on its surface and also allows the membrane liquid to enter into its pores. Spiral-wound and hollow-fiber supported liquid membrane have considerable higher surface areas of contact (104 m^2/m^3 [21]). SLM can be classified into two major type *i.e.*

(1) Flat sheet supported liquid membrane (FSSLM)

(2) Hollow fiber supported liquid membrane (HFSLM).

2.1.2.1. Flat Sheet Supported Liquid Membrane (FSSLM)

The flat sheet supported liquid membrane is the simplest form of SLM technique. A micro-porous flat solid support is used for the organic membrane. The solid porous support is impregnated with carrier and is fixed between two compartment using gaskets. One section is used for feed phase and the other compartment is for the strip phase solution. Both the phases are stirred by mechanical stirrers.

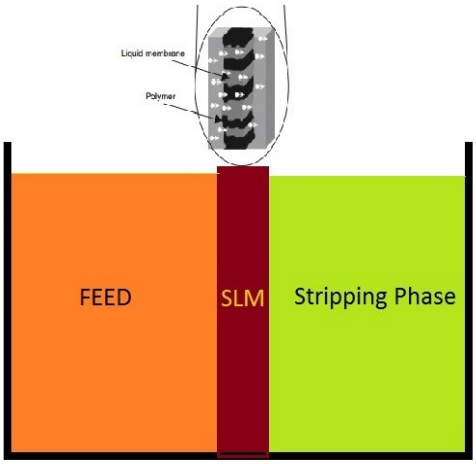

Figure 2.2 Schematic of FSSLM

2.1.2.2. Hollow Fiber Supported Liquid Membrane (HFSLM)

Hollow fibre supported liquid membrane is resemble to shell-tube heat exchanger. It often is used for removal of metal ions. The outside cell of the module is a single nonporous material through which the insider solution cannot be transported. Inside the shell, many thin fibres are packed in rows (Figure 2.3). The feed phase passes through the fibers on the other hand the strip phase passes through the shell side.

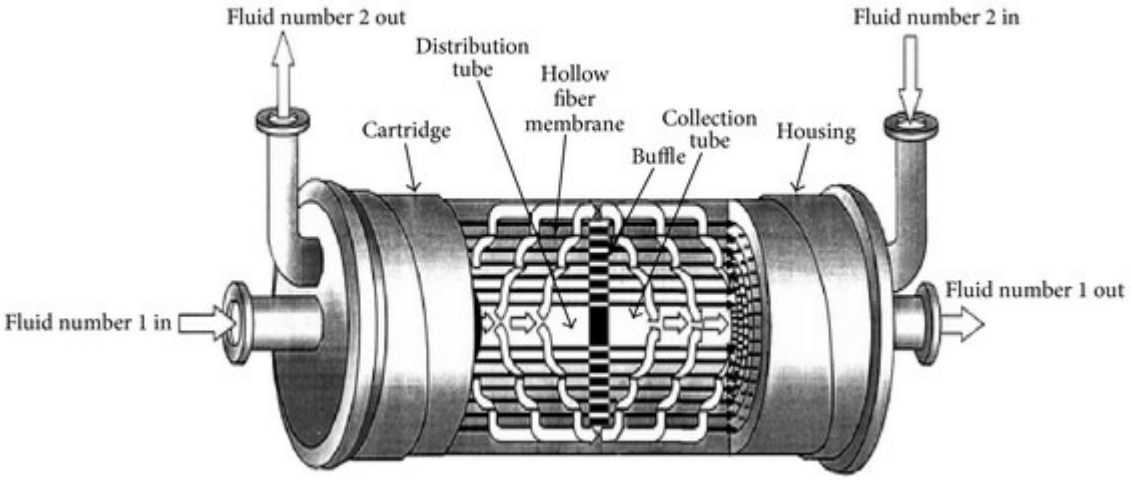

Figure 2.3 Schematic of HFSLM [22]

2.1.3. Emulsion Liquid Membrane:

After the discovery ELM technique by Norman Li in 1968, ELM gained importance among the conventional separation methods. ELM method has advantages over other separation method like permeable and semi-permeable membranes such as ultrafiltration, microfiltration and reversed osmosis due to high capital cost, large equipment size, low selectivity and low mass transfer rate. ELM offers some intensity features such as larger interfacial surface area, high efficiency and simple operation methods. The emulsion liquid membrane technique has great prospective for removal and recovery of different metal ions from wastewater, over the conventional separation methods. But ELM struggles for the emulsion instability, breakage of the membrane due to swelling during high shear rate and stress rate throughout the separation process, which affect the overall efficiency of the ELM processes.

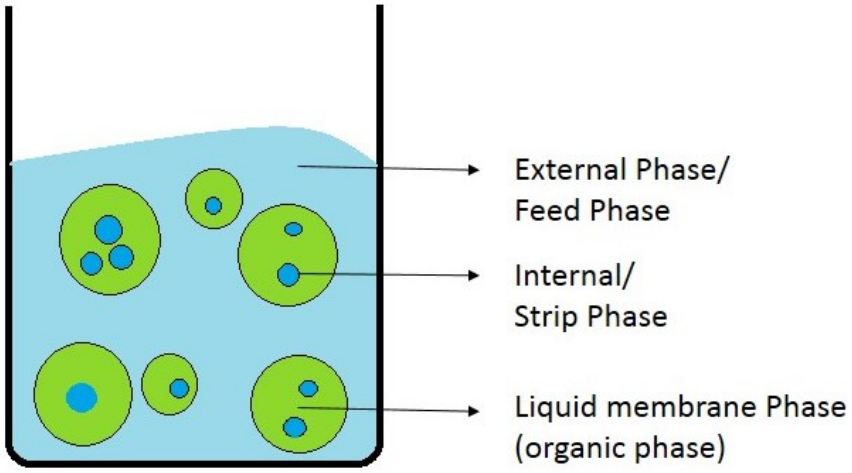

Figure 2.4 Schematic of ELM

The emulsion may be of two different types *viz.* water-in-oil emulsion and oil-in-water emulsion. In water-in-oil (W/O/W) type emulsion is the immiscible oil phase is act as membrane. The oil membrane phase separate the two aqueous phases i.e. feed and strip phases, while in the oil-in-water (O/W/O) type emulsion the immiscible water phase act as membrane separating the two organic phases. Figure 2.4 shows schematic picture of a w/o/w multiple emulsion and representation of the phases.

The emulsion system has a high interfacial area, 3000 m^2/m^3 compared to 100-200 m^2/m^3 for SLM [23]. The membrane thickness is very thin compare to other liquid membrane that's

why diffusivity through membrane is much higher than through other liquid membrane. ELM provides *high mass transfer flux* due to the potentials to incorporate chemical components, which improve the transport of the metal. *The extraction and the stripping coexist* in the same stage, which gives savings in the equipment volume.

The overall mass transfer controlled by a combination of the reaction rate and diffusion rate of the extractant and the metal complex. The volume of external phases much higher than that of internal phase that enables metal concentration in the internal phase.

The main disadvantage of ELM is the instability of emulsion globules. The breakage of globules occurs mainly by osmotic swelling. The osmotic swelling occurs when the aqueous phase diffuses through the membrane phase and swells the internal droplet, causing dilution of the content in the internal phase. This process involves *de-emulsification*, which involves the recovery of the membrane phase and the metal, is also a critical process. The de-emulsification process needs high voltage, which is an energy demanding process.

2.2. Applications of Liquid Membranes

Liquid membrane technology is gaining importance in various industrial applications due to its low cost, achieving high separation factor and ease of application. All three different LM techniques are being used in various industries and academic research work across the globe. The major application of liquid membrane is in the field of (a) Gas Separation, (b) Recovery of uranium and copper, (c) Nickel recovery from spent galvanic solutions, (d) Phenol removal, (e) Ammonium removal, (f) Applications in biochemistry etc. [24, 25].

The simplest of all forms of LM techniques is BLM technique. One disadvantage associated with BLM technique is their slow kinetics. However, it is very useful technique for evaluation of various process. Although separation of precious metals likes gold, silver etc. can be justified by BLM method.

2.3. Elements of Bulk Liquid Membrane

2.3.1. Carrier

Carrier is the most important component of liquid membrane. It is also known as extractant agent. Carrier is present in the membrane phase and is used to facilitate the metal-transport through the membrane. According to chemical behaviour of the carrier is broadly categorized into the three following types [26].

1) Acidic: Mainly organophosphinic acids (*i.e.* Cyanex 272, DTPA) and organophosphonic acids (*i.e.* PCA 88A, *Ionquest* 801) etc.

2) Basic: Quaternary ammonium salts (*i.e. Aliquat*336) and tertiary amines (*i.e.* TOA, TNOA, *Alamine* 336) etc.

3) Solvating extractants: Phosphorous esters (*i.e.* TBP) and phosphine oxides (*i.e.* TOPO, Cynaex 923) are included in this category

Performance of a liquid membrane is strongly co-related to the characteristics of a carrier. The main characteristics of carriers in liquid membrane transport are:

1. High selectivity towards the species (metal ion) has to be separated
2. High extraction efficiency.
3. Very fast rate of complexation with targeted substance from an aqueous feed phase into Liquid membrane phase at feed-LM interface (high partition coefficient or extraction)
4. Very fast de-complexation rate LM-Strip interface.
5. High Stability of the carrier
6. No degradation reactions
7. No side reactions
8. Solubility of the carrier in the aqueous phases should be negligible.
9. No toxicity
10. It should be easily regenerated

Carrier is promoting facilitated metal ion transport through the liquid membrane. Table 2.1 shows some earlier studies on metal ion extraction using several types of carrier.

Table 2.1 Type of carrier, stripping solution, external solution and diluents used in metal extraction using LM processes [21]

Carrier	Metal ion	Feed Solution	Stripping solution	Diluent
Cyanex 272, LIX 63	Cu	$CuSO_4$ Cu salt	6N H_2SO_4 HCl	Tetradecane Kerosene
Cyanex 272	Ni	$NiNO_3$	6N H_2SO_4	Tetradecane
D2EHPA		$NiCl_2$	HNO_3	Kerosene
PC-88A		$NiSO_4$	Dil H_2SO_4	n-Heptane
Cyanex 272/DEHPA	Zn	$ZnSO_4$	6N H_2SO_4	Tetradecane
D2EHPA		$ZnCl_2$	HNO_3	Kerosene
DEHMTPA		$ZnSO_4$	Thiourea	n-Dodecane
D2EHPA	Ag	$AgNO_3$	HNO_3	Toluene
D2EHPA	Pb	$Pb(NO_3)_2$	HCl	Toluene
PC-88A	Co	$CoSO_4$	H_2SO_4	Paraffin oil
MSP-8	Pd	Simulated Waste	H_2SO_4	n-Heptane
TOA	Hg, Cr	$HgCl_2$	NaOH	Toluene
Adogen	Cd	Pure Cd	NaOH	Dimethyl Benzene
Primene JMT	Ag	Ag salt	H_2SO_4	Tetradecane
Aliquat 336	Cr	Cr(IV)	NaOH	Kerosene

In this work *tri-n-octyl amine* has been chosen as carrier for this research work. TOA is tertiary amine with is a melting point of -39°C and viscosity of 8.325mPa·sat 298.15 K. As seen in Figure 2.5, TOA contains a basic nitrogen group with one lone pare electron, which contributes to a so-called complexation reaction between the carrier and the metal ion. This reaction is relatively fast in comparison to other complex formations *i.e.* ligand formation, this due to the presence of strong electrostatic interactions.

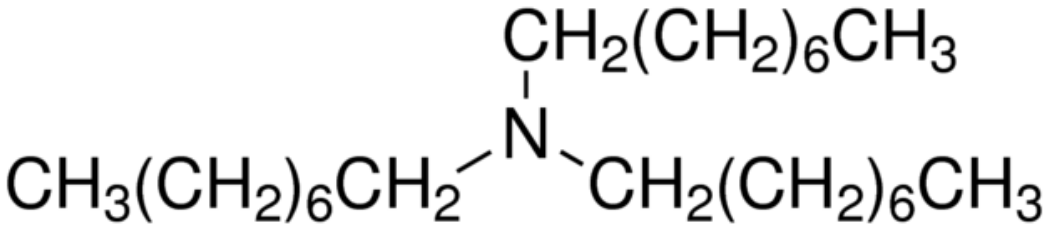

Figure 2.5 Chemical Structure of TOA

2.3.2. Diluent

Diluent is one of the key components of liquid membrane. It has an important function in the LM process. The stability of the membrane is a vital factor for an effective metal-transport. A diluent with higher viscosity can generally increase the liquid membrane stability but a high viscosity can also slow down the mass transport rate due to a higher diffusion resistance. Low solubility of diluent is highly required for success of BLM technique. For industrial use of the liquid membrane process, the diluent stands for the largest amount therefore other properties should also be considered such as corrosiveness, thermal and chemical stability, easy recoverability, and recyclability.

2.3.3. Stripping agents

Stripping phase is used for recovery of metal ions from membrane phase through a stripping reaction. This reaction converts the metal ion into a membrane insoluble compound hence metals ions trap into the stripping phase. It also enables transport against the metal concentration gradient. The stripping agent can be an acid or a base, depending on the specie to be extracted. As an example, NaOH, Na_2CO_3, KNO_3 can be used as stripping agent for the chromium removal from wastewater.

2.4. Transport Mechanism of Cr (VI) in BLM

The chromate ion has variety of forms ($HCrO_4^-$, $Cr_2O_7^-$, CrO_4^{2-}) in aqueous phase, depending upon the pH and abundance of the solution. For chromate concentration less than 1.76×10^{-2} mol/L (≈ 5000 ppm) [27], $Cr_2O_7^{2-}$ and $HCrO_4^-$ anion predominates in acidic pH

while in basic pH, CrO_4^{2-} predominates. Thus in this study, it may be concluded that $HCrO_4^-$ anion would exist in feed phase.

Alkyl amine has been reported as one of the best known carrier for Cr (VI) separation. These amines are generally water insoluble in nature. Presence of a basic nitrogen atom makes it affinitive towards variety of inorganic and organic acids. It forms complexes with chromate ions. The general reaction is shown below:

Feed phase reaction

$$(R_3NH{+}Cl^-)_{(org)} + HCrO_4^-{}_{(org)} \Leftrightarrow (R_3NH^+, HCrO_4^-)_{(org)} + Cl^-(aq) \qquad (2.1)$$

The chromate-TOA moiety as is formed above is diffused through the membrane/strip phase interphase to the stripping phase. In stripping phase the following reaction is expected to take place.

Strip Phase Reaction

$$(R_3NH^+, HCrO_4^-)_{(org)} + 2NaOH_{(aq)} \Leftrightarrow R_3N_{(org)} + CrO_4^{2-}Na_2^+ + 2H_2O \qquad (2.2)$$

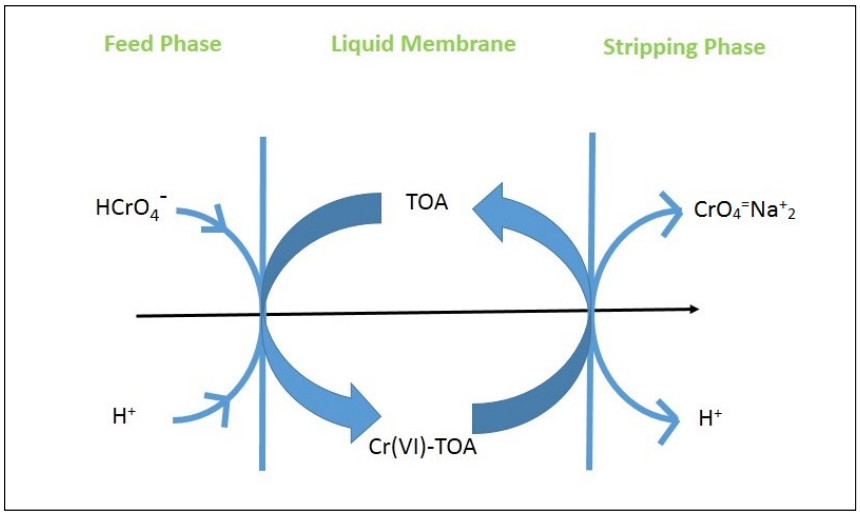

Figure 2.6 Kinetic scheme of chromate ion in BLM

2.5. Kinetic Model of Bulk Liquid Membrane

The mass transfer model of BLM is quite simple. An organic membrane containing a carrier makes a barrier between two aqueous phases (feed, strip phase). A specific solute, diffuse from the bulk feed solution to the Feed/Membrane interface, and is extracted from feed phase, due to complexation with carrier. The solute or solute-LM complex diffusing to the

Membrane/Strip interface is simultaneously de-complexed and stripped by the stripping phase. Transportation of solute occurs in BLM by the following steps

1. Diffusion of solute through the bulk feed solution to the Feed/LM interface.

2. Absorption on the Feed/LM interface.

3. Convective transport of solute within the membrane.

4. Diffusion through the boundary layer on the stripping side,

5. Desorption on the membrane/stripping solution interface,

6. Diffusion through the boundary layer to bulk stripping solution.

Kinetics of liquid membrane transport is controlled by both the diffusion rate of the various species and the kinetics of the various chemical reactions occurring in the system. To specify the exact mass transfer mechanism several models have been investigated. The chemical kinetic approach is one of the best model for establishing the transport mechanism of BLM. The nonsteady-state kinetic model has to be considered and more extensive kinetic analysis is necessary for BLM transport.

To depict the change of Cr(VI) ion concentration in three phases, the dimensionless reduced concentrations (*R*) has been used due to the ease of representation. Concentration of two aqueous phases is finding out by spectrophotometric method whereas membrane phase concentration has been calculated by total mass balance. The total mass of chromate ion has been balanced with respect to the reduced concentrations can be expressed as

$$R_F + R_M + R_S = 1$$

$$R_F = C_F/C_0,\ R_M = C_M/C_0,\ R_S = C_S/C_0$$

Where C_0 is the initial chromate ion concentration in the feed phase. C_F, C_M and C_S represent the chromate ion concentration in feed, membrane and stripping phases, respectively. The experimental results recommend that the Cr(VI) ion transport follows the kinetic laws of two successive irreversible first-order reaction in series according to the following kinetic scheme [28]:

$$C_F \xrightarrow{k_1} C_M \xrightarrow{k_2} C_S \quad (2.3)$$

Where k_1 and k_2 represent os pseudo-first-order reaction rate constants of the extraction and stripping, respectively. The above kinetic scheme (Equation 2.3) can be defined by the following set of equations

$$\frac{dR_F}{dt} = -k_1 R_F = J_F \quad (2.4)$$

$$\frac{dR_M}{dt} = k_1 R_F - k_2 R_M \quad (2.5)$$

$$\frac{dR_S}{dt} = k_2 R_M = J_S \quad (2.6)$$

Where J represents the flux. Integration of equations 2.4–2.6 gives the following expressions:

$$R_F = exp(-k_1 t) \quad (2.7)$$

$$R_M = \frac{k_1}{k_2 - k_1}\left[exp(-k_1 t) - exp(-k_2 t)\right] \quad (2.8)$$

$$R_S = 1 - \frac{1}{k_2 - k_1}\left[k_2\, exp(-k_1 t) - k_1 exp(-k_2 t)\right] \quad (2.9)$$

Concentration of feed phase decrease simultaneously strip phase concentration increases. From the experimental curve it was found that R_M has a maximum (for $dR_M/dt = 0$). From which the calculation of maximum values of chromium concentration in the membrane phase can be done by the following equations:

$$R_M = \left(\frac{k_1}{k_2}\right)^{-k2/(k1-k2)} \quad (2.10)$$

$$t_{max} = \left(\frac{1}{k_1 - k_2}\right) \ln\left(\frac{k_1}{k_2}\right) \quad (2.11)$$

From equation 2.8 and 2.9 the following relationship can be derived

$$k_2 = \frac{\ln(1 / R_{Mmax})}{t_{max}} \quad (2.12)$$

The initial value of $k_1$was obtained by curve fitting from equation 2.7 with MATLAB (2014b) software. The initial value of k_2 was found from equation 2.12. By differentiation of equation 2.8–2.9 at t_{max}, the following equations were obtained:

$$\frac{dR_F}{dt}_{max} = -k_1\left(\frac{k_1}{k_2}\right)^{-k1/(k1-k2)} \equiv J_{F\,max} \quad (2.13)$$

$$\frac{dR_M}{dt}_{max} = 0 \quad (2.14)$$

$$\frac{dR_S}{dt}_{max} = k_2\left(\frac{k_1}{k_2}\right)^{-k2/(k1-k2)} \equiv J_{S\,max} \quad (2.15)$$

The system is in a steady state at $t = t_{max}$, because the concentration of chromate ion in the liquid membrane does not change with time. Thus both fluxes, i..e entrance and exit, are equal and have opposite signs thus $-J_{F}max = J_{S}max$.

2.6. Factor affecting the performance of Bulk Liquid membrane

2.6.1. Membrane formulation

The membrane phase consists of diluent, carrier and requires an optimal formulation for the BLM to be stable and for the extraction to take place. Selection of suitable formulation is very important for successful metal ion transport carrier. Because each carrier is selective for certain metal ions.

2.6.2. Stirring rate

The stirring has a large impact on the BLM extraction capacity, since it enhances the mixing during extraction and provides higher mass transfer rate. Starring is require for faster Cr(VI) transportation. With increase stirring rate convective mass transfer rate increase to an upper limit. However, a further increase in stirring speed may lead to a decrease in membrane stability. In this study stirring rate was kept constant at 100rpm.

2.6.3. Carrier Concentration

Carrier concentration in liquid membrane have significant influence in transport efficiency. The main function of carrier to transport selectively the targeted metal ion through liquid membrane. It is general trend that effectiveness of membrane transport increase as carrier concentration increases and get saturated at some point, onward carrier concentration does not affect the transport kinetics further

2.6.4. Stripping agent concentration

The stripping agent concentration has an imperative role when it comes to the stripping rate. Stripping rate increase as concentration increases to the stronger pH gradient and the higher amount of stripping agent present. The difference in pH between the feed phase and the stripping phase is the chief driving force for the transportation of the carrier-metal complex through the liquid membrane phase. Previous study exhibited that an optimal stripping agent concentration exists and a further increase has a negative influence on the stripping

efficiency. Numerous number of stripping has been reported. NaOH, Na_2CO_3, $NaHCO_3$ KOH, H_2SO_4etc are the common stripping agent.

2.6.5. Metal concentration of the feed phase

The metal ion concentration in the feed phase influences both the extraction rate and efficiency. High initial metal concentration requires a high extraction capacity and a low initial metal concentration means that the metal ions may have to compete with other ions present in the feed phase.

2.6.6. pH of the Feed phase

pH of feed phase make important impact in order to accomplish the extraction of metal ion from water. Moreover, pH of feed phase control the structure of the different metal complexes in the feed phase influence the carrier-metal transport.

CHAPTER 3

EXPERIMENTAL WORK

3.1. Chemicals

All chemicals used in this experiment were of analytical grade. *Tri-n-octyl amine* (TOA), *dioctylamine* (DOA), *tri-iso-octylamine (TIOA)*, *Aliquat-336* was purchased from Sigma-Aldrich (India). *1, 2-dichloroethane*, NaCl, Na_2SO_4, KNO_3, NaOH, $NaHCO_3$ were supplied from Fisher Scientific (India). $K_2Cr_2O_7$ was obtained from Merck (Germany). All aqueous solutions were prepared using Milli-Q deionised water (Millipore, USA). A detailed list of inventory is given below:

Table 3.1 List of Chemicals used in Experiment

Chemical	Supplier	Purity (%)	Molecular weight (g/mole)	Density at 25°C(g/ml)	Viscosity (mPa.s)	b.p. (^OC)
1,2-dichloro ethane	Fisher Scientific (India)	99	98.96	1.25	0.8	81-85
dioctylamine (DOA)	Sigma-Aldrich (India)	98	241.46	0.799		297
tri-iso-octylamine (TIOA)	Sigma-Aldrich (India)	98	353.67	0.816		365
tri-n-octlamine	Sigma-Aldrich (India)	98	353.67	0.809		365-367
Aliquat-336	Sigma-Aldrich (India)		442	0.884	1450	
NaCl	Fisher Scientific (India)	99	58.44			
Na2SO4	Fisher Scientific (India)	99	142.04			
KNO_3	Fisher Scientific (India)	99	101.1			
NaOH	Fisher Scientific (India)	97	40			
$NaHCO_3$	Fisher Scientific (India)	99.7	84.01			
$K_2Cr_2O_7$	Merck (Germany)		294.185			
HCL	Fisher Scientific (India)		36.46			

3.2. Analytical Instrument

For measuring concentration of different phases, UV-visible spectroscopy method was used (JASCO V-750 model). pH measurements of aqueous phases were carried out by pH meter. All experiments were carried out at 25 ± 2^{o}C. For measuring concentration of different phases, samples (3ml) from the each aqueous phase were taken periodically and analyzed. UV-vis spectroscopy is one of the most convenient ways for determining concentrations [Cr (VI), in this study]. Uses of coupled plasma (ICP-OES and ICP-MS) spectrometry and atomic absorption spectrophotometry (AA) are also frequently used for determining chromate ion concentrations.

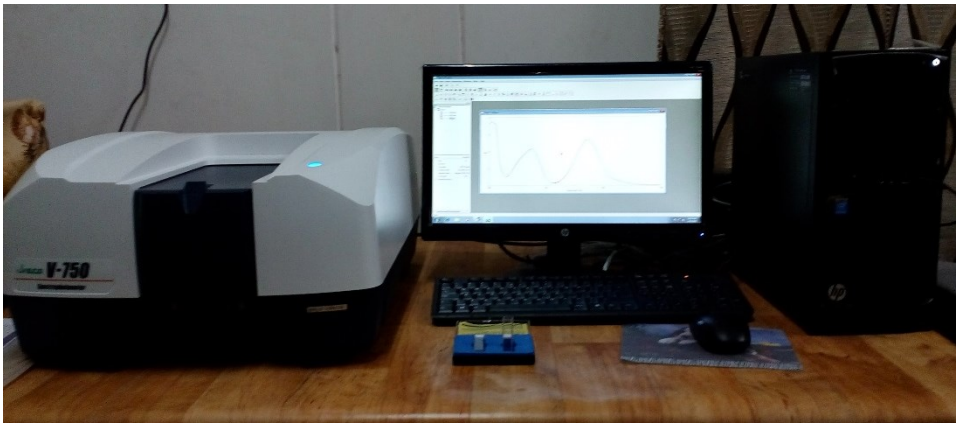

Figure 3.1 Photograph of JASCO (V-750) UV-vis spectrophotometer

The concentration is measured with UV-Vis spectroscopy using the Beer-Lambert law, which states that: when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation is proportionally dependent on thickness of the absorbing solution well as the concentration of the solution.

The expression for Beer-Lambert law is:

$$A = \log (I_0/I) = \varepsilon \times c \times l \qquad (3.1)$$

Where, A = absorbance
I_0 = intensity of light incident upon sample cell
I = intensity of light leaving sample cell
L = length of sample cell (cm.)
Ɛ= molar absorptivity
C = molar concentration of solute

From the Beer-Lambert law it is clear that higher concentrated solution is capable of absorbing greater the extent of light of a given wavelength. This is the basic principle of UV spectroscopy.

Firstly calibration curve is established with known concentration, 50, 100, 150, 200 ppm, of Cr (VI) ions. The calibration curves obtained of chromium can be seen in Figure: 3.2. Concentration of samples was found by comparing its UV absorbance with standard curve.

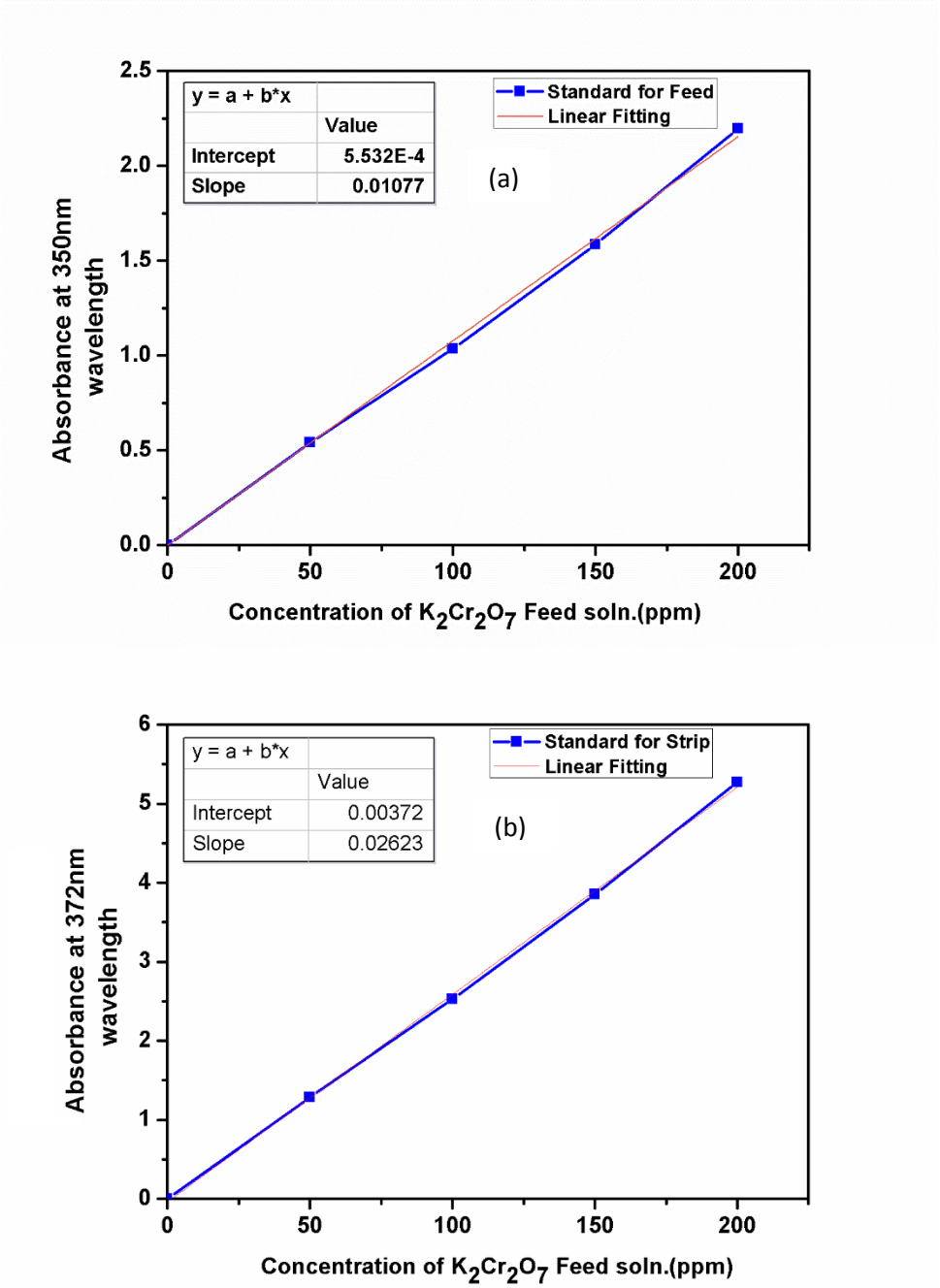

Figure 3.2 Calibration Curve for a) Feed phase b) Strip Phase

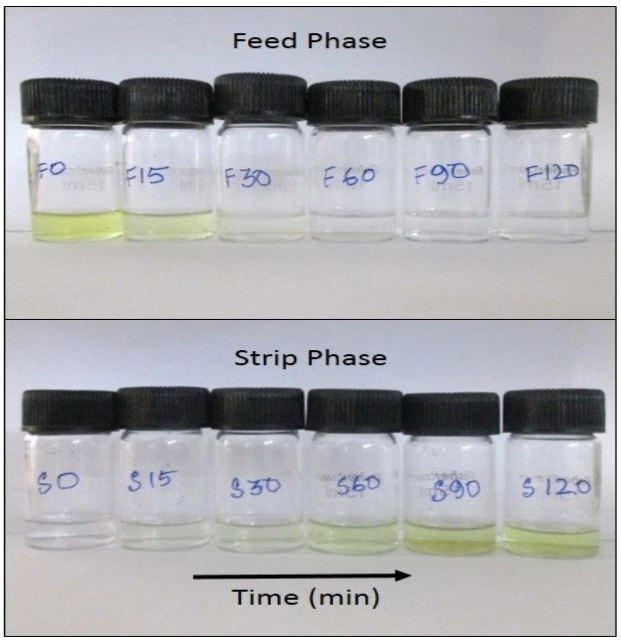

Figure 3.3 Colour change of samples with time for feed and strip

3.3. Experimental Setup

A typical bulk liquid membrane setup has two separate compartments; out of which one is used for donor or feed phase and the other one is used for receiving or stripping phase. Glass being non-reactive to most of the chemicals and its transparency allows clear visualization of the in-situ effects as the transport occurs was the preferred material of construction for this BLM ensemble. During conceptualization, the dimensions of the proposed fabricated setup were carefully made so as to avoid minimum wastage of expensive chemicals, particularly since it involves series of trial and errors during experimentations. The dimension of the BLM module is: 10 cm (height) × 8 cm (width) × 4 cm (breadth) respectively (Figure 3.4). 150 ml of both the aqueous phases were taken in separate compartments after pouring the organic liquid membrane phase (*1, 2-dichloroethane*) in the module. The organic liquid membrane (LM) phase is comprised of a diluent and carrier and its density *w.r.t* source and strip phase determines its positioning in the module. In this study, the LM connects source and strip phase via the passage at the bottom, owing to its heavier density (1.254 g/ml).

Organic solvent is the major constituent of the membrane phase and its stability is a vital factor for an effective transport. Since a low viscosity of the solvent or diluent benefits the overall efficiency of bulk liquid membrane as it decreases the mass-transfer resistance and thereby increases the mass transfer coefficient, in this study *1, 2-dichloroethane* was the preferred organic solvent as the LM. Precautions were taken to prevent mixing of feed and strip phase. It was assured that the upper level of membrane was kept above the bottom clearance of the separating plate. Both aqueous phases were stirred continuously by two impeller type motor driven stirrer. The speed of stirrer was kept constant at 100 rpm throughout the course of the study. Sampling was done from both aqueous phases periodically to determine the change in Cr (VI) concentration.

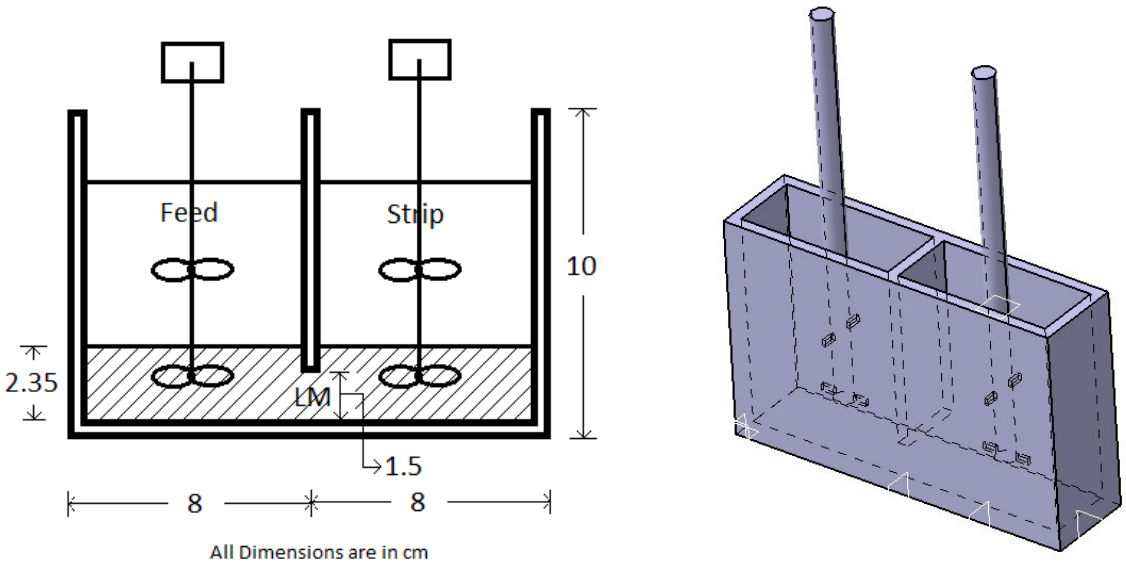

Figure 3.4 Schematic diagram of Bulk Liquid membrane setup

CHAPTER 4

RESULTS & DISCUSSION

In the following paragraphs the details of our experimental findings are narrated.

4.1. Selection of Carrier

As carrier plays an important role in extraction and stripping of Cr (VI) ions thus selection of carrier is very crucial for success of liquid membrane technique. Carrier should have the inherent property of rapid kinetics of formation (complexation) and destruction (decomplexation) around the membrane interfaces.

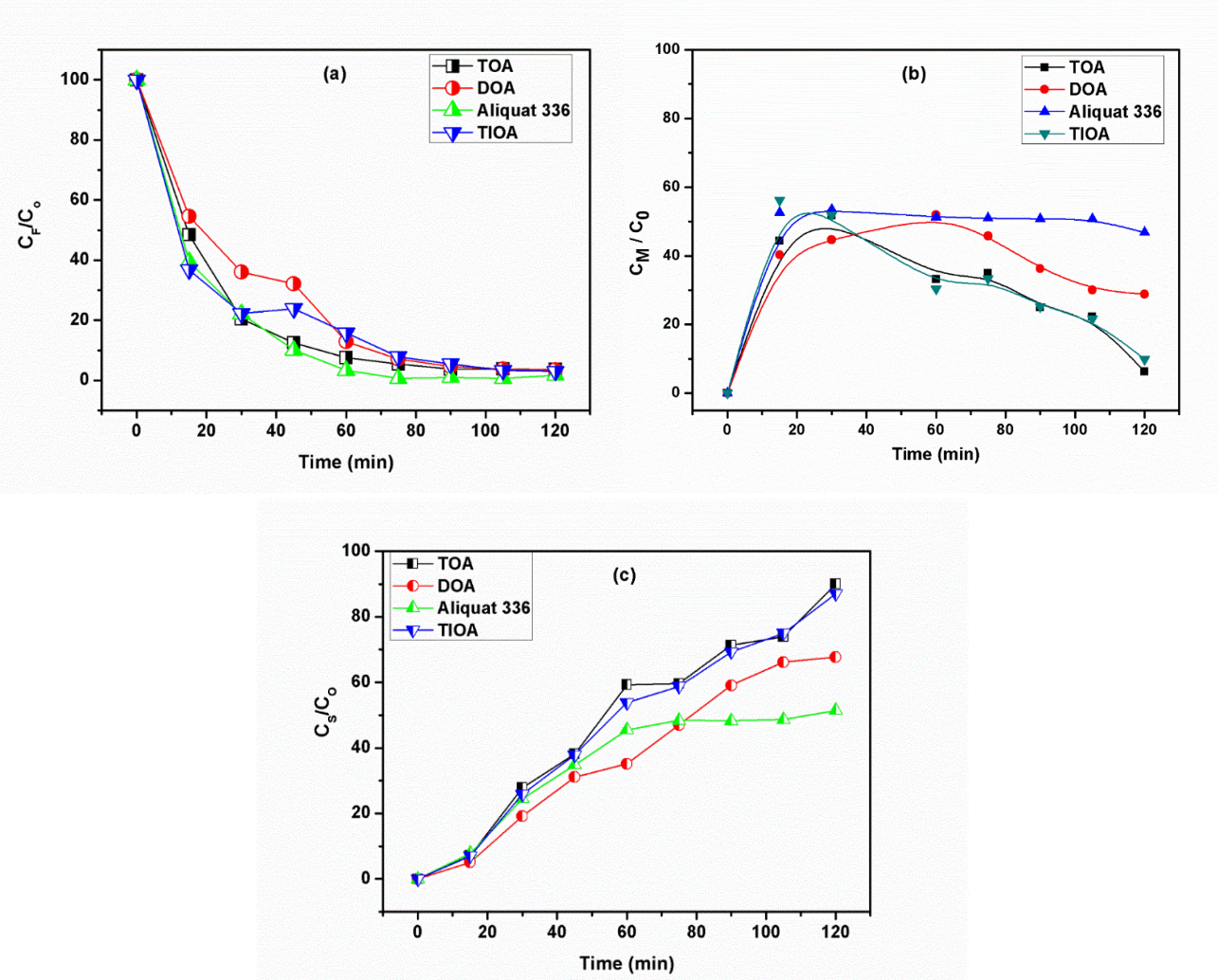

Figure 4.1 Selection of Carrier: % Cr (VI) concentration in (a) feed, (b) membrane and (c) stripping phase as a function of time. (Experimental condition: Feed solution: $[K_2Cr_2O_7]$ = 200ppm, Carrier Loading= 1 vol. %, Strip phase concentration: 0.1 N NaOH, pH of feed phase = 1)

A comparative assessment on four different types of alkyl amine carriers yielded interesting results. Figure 4.1 depicts the kinetics of the complete transport process. From figure 4.1 (a) it is clear that both Aliquat-336 and TOA shows faster extraction kinetics (from source phase to LM) as compared to DOA and TIOA. However, the kinetics during the stripping process (from LM to strip phase) as is shown in figure 4.1(b, c) for Aliquat-336 is slower than TOA. Since, TOA showed a consistent faster kinetics in both extraction and stripping *vis-a-vis* other amines, it was the preferred carrier.

Table 4.1 The change of kinetic parameters during transport of Cr (VI) ions with different carriers

Carrier	t_{max}(min)	R_M max	k_2 (min^{-1})	k_1(min^{-1})	J_F max (min^{-1})	J_S max (min^{-1})	% Recovery
TOA	30	0.517	0.021	0.047	−0.011	0.011	89
DOA	30	0.447	0.026	0.031	−0.010	0.010	67
Aliquat-336	45	0.551	0.013	0.552	−0.012	0.012	51
TIOA	30	0.562	0.019	0.043	−0.010	0.010	87

(Experimental condition: Feed solution: [$K_2Cr_2O_7$] = 200ppm, Carrier Loading = 1 vol. %, Strip phase concentration: 0.1 N NaOH, pH of feed phase = 1)

Variation of kinetic parameter of Cr(VI) of different carrier have been presented in table1. TOA and Aliquat-336 shows highest transport rate k_1 but k_2 value for TOA is much higher.

4.2. Effect of Carrier concentration

The carrier concentration in the organic membrane phase has a substantial effect on the metal ion transport. The main function of carrier is to transfer selectively the targeted metal ion through the liquid membrane. It is a general trend that effectiveness of membrane transport increases as carrier concentration increases and gets saturated at some point and after that carrier concentration does not affect the transport kinetics further. In some study it has been reported excess carrier (TOA) concentration hinders diffusion rate as viscosity of membrane increases [29].

To examine the effect of carrier concentration on transport kinetics, experiments were carried out with six different carrier concentrations (i.e. 0.1, 0.25, 0.5, 1.0, 2.0 and 3.0 vol. %). In these set of experiments, it was observed that the effectiveness increased with an increase in carrier concentration (Figure 4.2) up to a vol. % of *ca*. 1. However, further increase in carrier concentration beyond that didn't rapid the extraction kinetics. The rate of increase did slow down gradually at higher concentration. It could be inferred that when carrier concentration ranged from 0.1 vol. % to 1 vol. %, the mass transfer rate of chromate ion was controlled by rate of complexation between Cr (VI) and TOA at feed/membrane interphase.

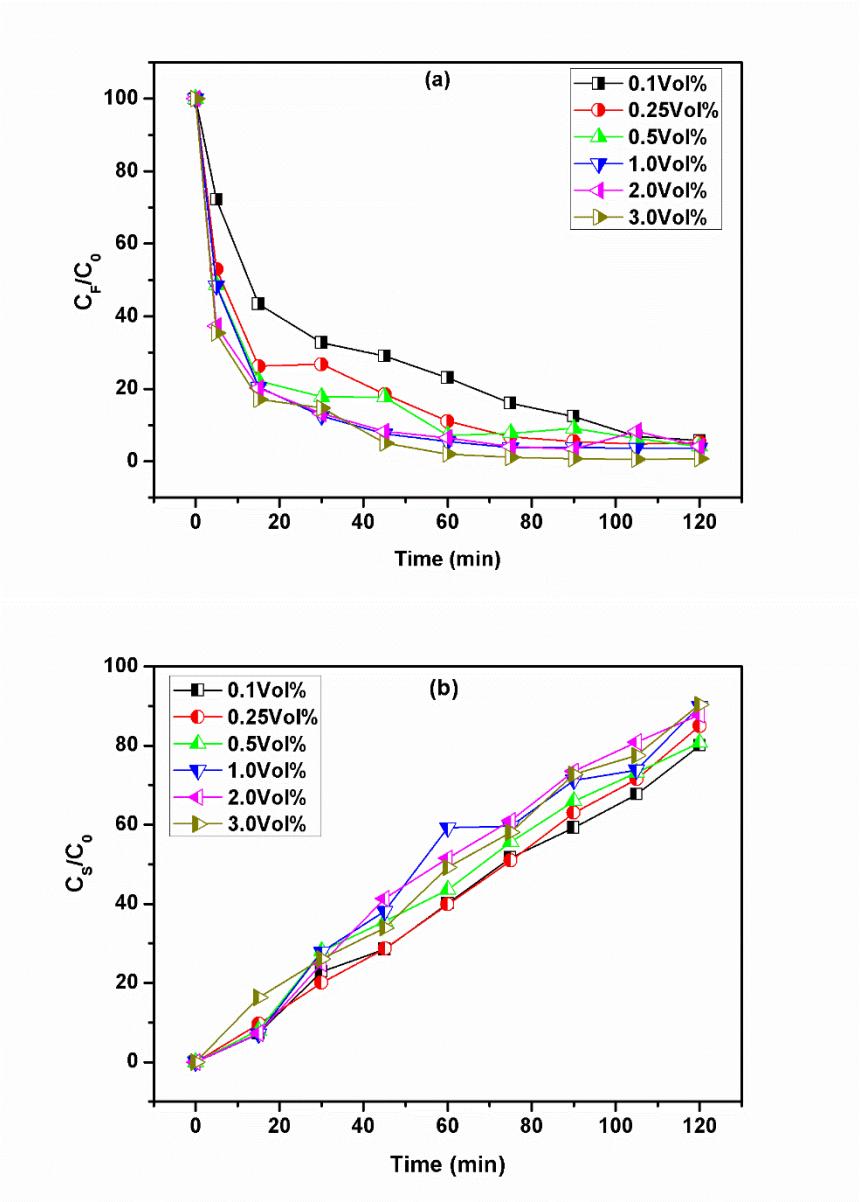

Figure 4.2 Effect of Carrier concentration: % Cr (VI) concentration in (a) feed and (b) stripping phase as a function of time. (Experimental condition: Feed solution: $[K_2Cr_2O_7]$ = 200ppm, Strip phase concentration: 0.1 N NaOH, pH of feed phase = 1)

Table 4.2 The change of kinetic parameters during transport of Cr (VI) ions with carrier concentration

Carrier Concentration (vol%)	t_{max}(min)	R_M max	k_2(min^{-1})	k_1(min^{-1})	J_F max (min^{-1})	J_S max (min^{-1})	% Recovery
0.1	45	0.387	0.021	0.021	−0.007	0.007	80
0.25	30	0.537	0.020	0.033	−0.009	0.009	84
0.5	30	0.497	0.023	0.040	−0.010	0.010	80
1	30	0.517	0.021	0.047	−0.011	0.011	89
2	15	0.552	0.039	0.053	−0.016	0.016	87
3	15	0.037	0.048	0.059	−0.011	0.011	90

(Experimental condition: Feed solution: [$K_2Cr_2O_7$] = 200ppm, Strip phase concentration: 0.1 N NaOH, pH of feed phase = 1)

As carrier concentration was increased, flux remained constant at the feed/membrane interphase, however, now the transport kinetics was controlled by decomplexation of chromate-TOA moiety at membrane/strip interphase which concurrently was impeded by the presence of excess carrier in the diffusion path.

4.3. Selection of Stripping Phase

Stripping phase selection plays an important part in success of LM technique. Generally basic solution is used for stripping phase and in this study the performances of various stripping phases were studied *viz*. aqueous solutions of NaOH, Na_2CO_3, Na_2SO_4, KNO_3 and NaCl where the membrane phase was 1, 2-dichloroethane (solvent) and TOA (carrier). The experimental results are shown in Figure 4.3 Aqueous NaOH showed the most promising result in terms of faster kinetics which can be attributed to its faster rate of decomplexation reaction at the membrane/strip interphase.

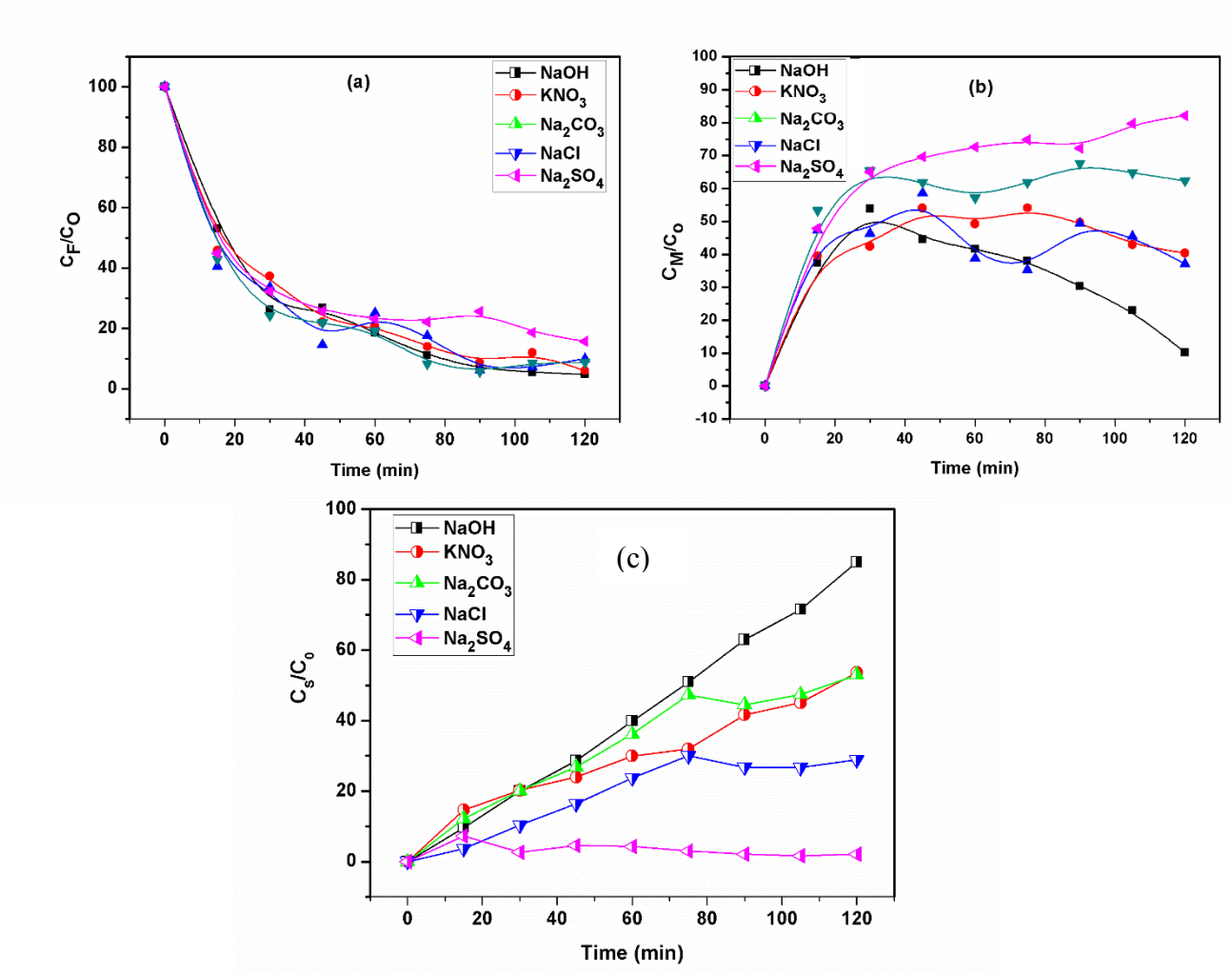

Figure 4.3 **Selection of Stripping Phase:** % Cr (VI) concentration in (a) feed, (b) membrane and (c) stripping phase as a function of time. (Experimental condition: Feed solution: [$K_2Cr_2O_7$] = 200ppm, TOA concentration= 0.25 vol. %, pH of feed phase = 1, Strip phase concentration = 0.1N)

Table 4.3 The change of kinetic parameters during transport of Cr (VI) ions with different stripping agent

Stripping agent	t_{max}(min)	R_M max	k_2(min^{-1})	k_1(min^{-1})	J_F max (min^{-1})	J_S max (min^{-1})	% Recovery
NaOH	30	0.537	0.021	0.033	−0.009	0.009	84.97
KnO_3	45	0.539	0.014	0.030	−0.007	0.007	53.58
Na_2CO_3	45	0.470	0.016	0.033	−0.008	0.008	52.94
NaCl	90	0.675	0.004	0.038	−0.003	0.003	28.86
Na_2SO_4	120	0.821	0.001	0.021	−0.001	0.001	2.10

(Experimental condition: Feed solution: [$K_2Cr_2O_7$] = 200ppm, TOA concentration= 0.25 vol. %, pH of feed phase = 1, Strip phase concentration = 0.1 N NaOH)

4.4. Effect of stripping phase concentration

The dependency of stripping efficiency on the strip phase concentration was also investigated by varying NaOH concentration in the range from 0.1-0.5 N. It could be concluded from Figure 4.4 that an increase in NaOH concentration facilitated the Cr (VI) transport and at 0.3 N, the recovery was optimum. It was also observed that higher NaOH concentration did not yield proportionate results in terms of Cr (VI) recovery largely due to much reduced driving force [30].

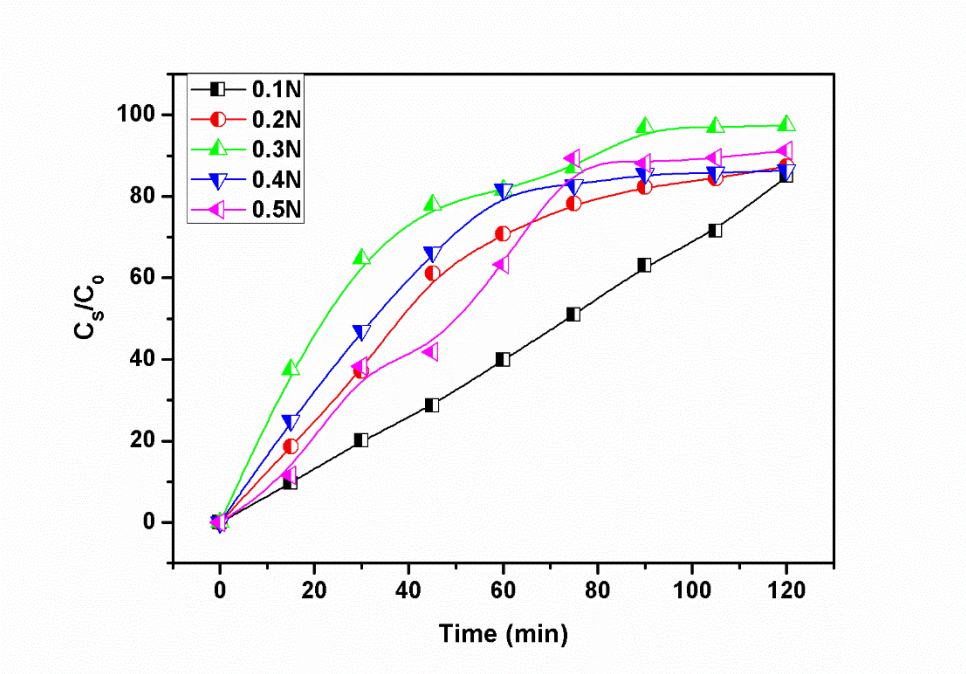

Figure 4.4 Effect of stripping phase concentration: % Cr (VI) concentration in stripping phase as a function of time. (Experimental condition: Feed solution: [$K_2Cr_2O_7$] = 200ppm, TOA concentration= 0.25 vol. %, pH of feed phase = 1)

Table 4.4 The change of kinetic parameter of Cr (VI) ions with stripping phase concentration

NaOH Conc. (N)	t_{max}(min)	R_M max	k_2(min^{-1})	k_1(min^{-1})	J_F max (min^{-1})	J_S max (min^{-1})	% Recovery
0.1	30	0.537	0.020	0.033	−0.009	0.009	84.97
0.2	15	0.410	0.059	0.044	−0.018	0.018	87.37
0.3	15	0.205	0.105	0.053	−0.026	0.026	97.42
0.4	30	0.283	0.042	0.049	−0.016	0.016	86.36
0.5	30	0.472	0.024	0.044	−0.014	0.014	91.24

(Experimental condition: Feed solution: [$K_2Cr_2O_7$] = 200ppm, TOA concentration= 0.25 vol. %, pH of feed phase = 1)

4.5. Effect of pH of Feed Phase

To understand effect of the feed phase pH on the extraction efficiency, pH was varied from 1-4 where pH was maintained by adding HCl drop wise to the feed phase. Maximum extraction was occurred when the pH of feed phase was set at 1 (Figure 4.5). As pH value was increased, the transport rate of chromate ion subsequently decreased due to incomplete protonation of TOA moieties in the feed/membrane interphase. It might be inferred that at low pH (~1), the most suitable complexation between TOA and Chromate ions occurred, facilitating the transport.

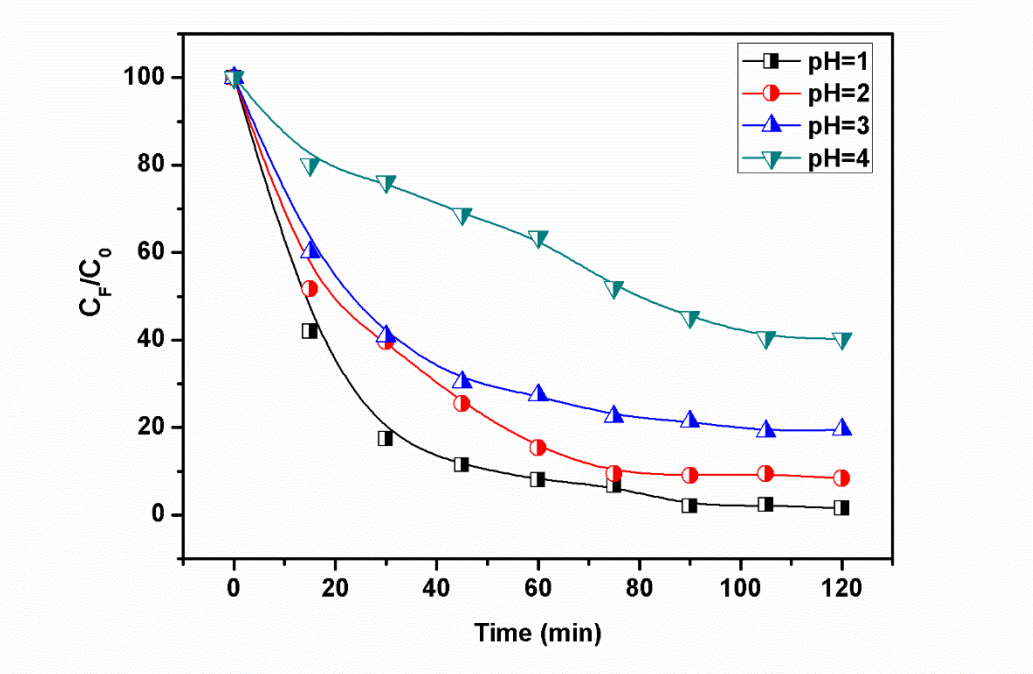

Figure 4.5 Effect of pH of Feed Phase: Cr (VI) concentration in feed phase as a function of time. (Experimental condition: Feed solution: $[K_2Cr_2O_7]$ = 200ppm, TOA concentration= 0.25 vol. %, Strip phase concentration: 0.3 N)

Table 4.5 The change of kinetic parameter of Cr (VI) ions with feed phase pH

pH	t_{max}(min)	R_M max	k_2(min^{-1})	k_1(min^{-1})	J_F max (min^{-1})	J_S max (min^{-1})	% Recovery
1	15	0.205	0.105	0.053	−0.026	0.026	97.42
2	30	0.152	0.062	0.030	−0.015	0.015	91.54
3	45	0.183	0.037	0.019	−0.009	0.009	75.10
4	75	0.248	0.014	0.008	−0.003	0.003	42.19

(Experimental condition: Feed solution: $[K_2Cr_2O_7]$ = 200ppm, TOA concentration= 0.25 vol. %, Strip phase concentration: 0.3 N NaOH)

4.6. Effect of Feed phase concentration

The influence of varying feed phase concentration on membrane performance was also investigated in the concentration range between *ca*. 50-400 mg/L (or, ppm). Figure 4.6 shows that for low feed phase concentration, 80% extraction was complete within 30 minutes of the start of the experiment whereas it took approximately 90 minutes for 400 ppm feed phase concentration. A slower transfer kinetics for higher concentration range perhaps could be attributed to the fact that membrane phase quickly got saturated with the Chromate ions affecting mass transfer in the feed/membrane interphase.

Table 4.6 The change of kinetic parameter of Cr (VI) ions with different feed phase concentration

$K_2Cr_2O_7$ Concentration (ppm)	t_{max}(min)	R_M max	k_2(min^{-1})	k_1(min^{-1})	J_F max(min^{-1})	J_S max(min^{-1})	% Recovery
400	15	0.157	0.123	0.031	−0.019	0.019	93.68
200	15	0.205	0.105	0.053	−0.026	0.026	97.42
100	15	0.372	0.065	0.053	−0.021	0.021	97.75
50	15	0.341	0.071	0.060	−0.024	0.024	96.01

(Experimental condition: TOA concentration= 0.25 vol. %, Strip phase concentration: 0.3 N NaOH, pH of feed phase = 1

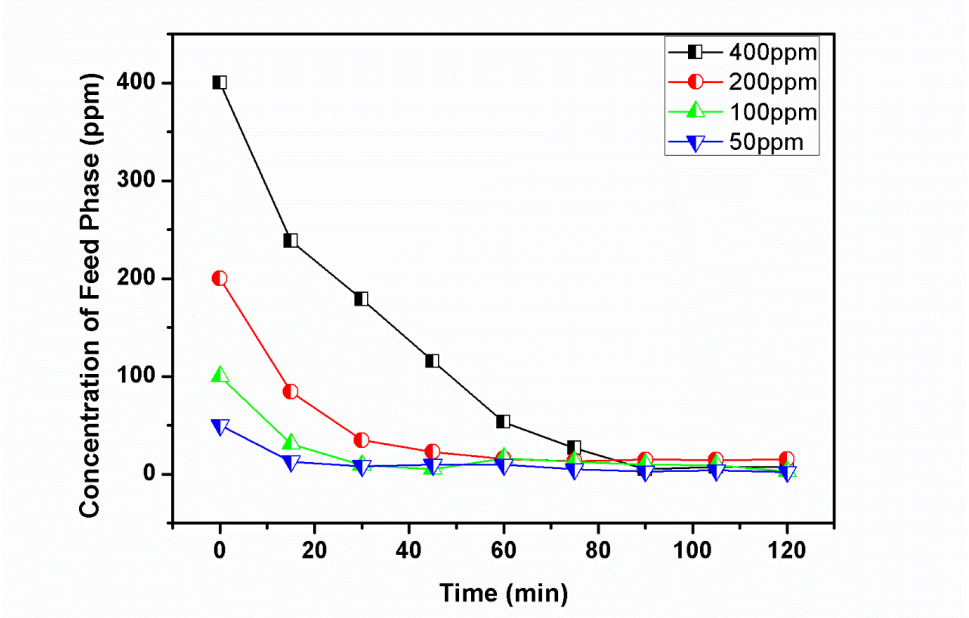

Figure 4.6 Effect of Feed phase concentration: Cr (VI) concentration in feed phase as a function of time. (Experimental condition: TOA concentration= 0.25 vol. %, Strip phase concentration: 0.3 N NaOH, pH of feed phase = 1)

4.7. Reusability of membrane

Reusability of membrane is also important factor for the success of bulk liquid membrane technique. In this study the membrane reproducibility had been checked four times after various runs. Utmost care was taken while separating the membrane phase to minimize the volume loss. Figure 4.7 clearly shows that the performance of the liquid membrane remains intact without any major deviation even after four-fold use.

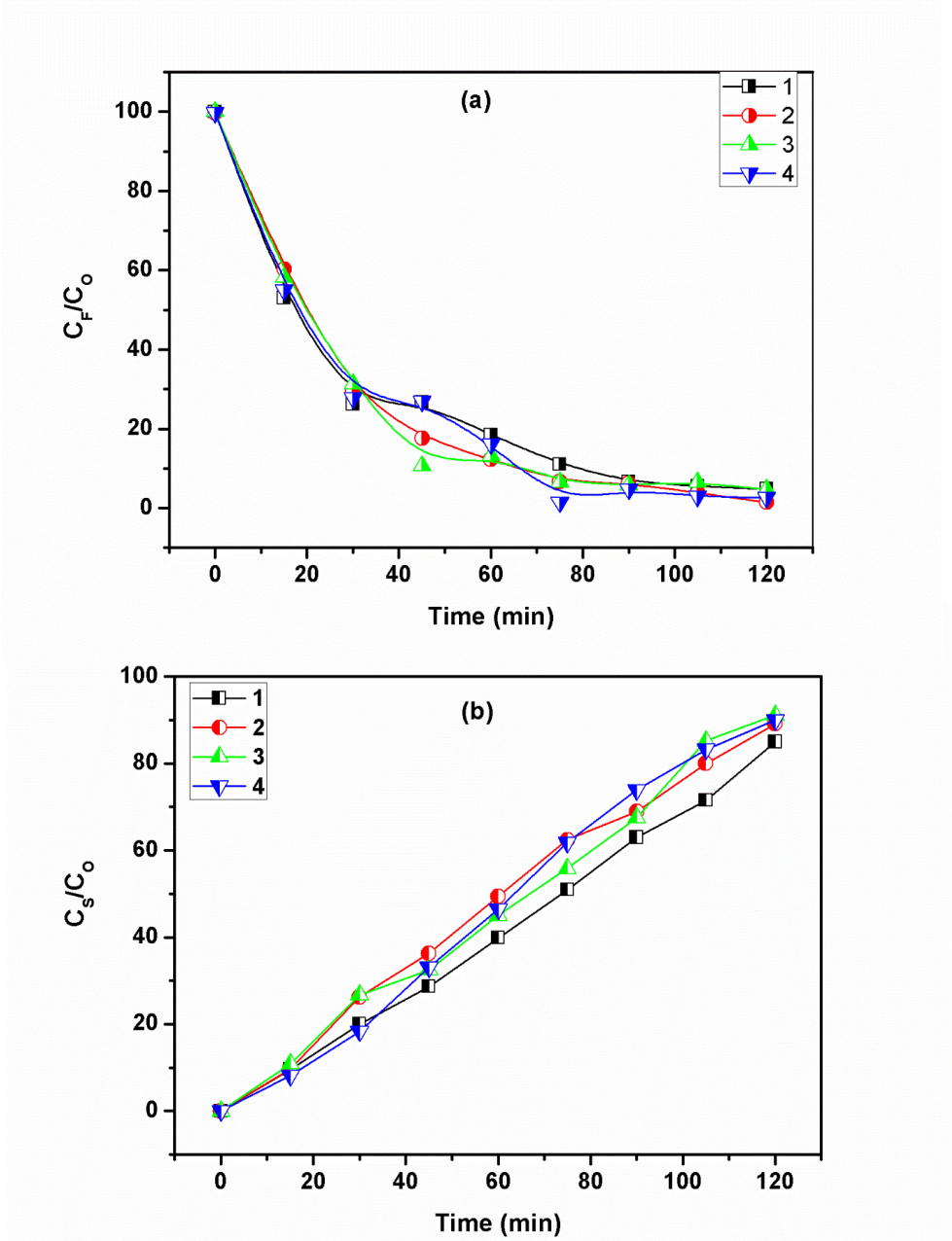

Figure 4.7 Reusability of membrane: Cr (VI) concentration in (a) feed and (b) stripping phase as a function of time. (Experimental Condition: Feed solution: [$K_2Cr_2O_7$] = 200ppm, Carrier Loading= 0.25 vol. %, Strip phase concentration: 0.1 N NaOH, pH of feed phase = 1)

CHAPTER 4

CONCLUSIONS AND FUTURE SCOPE

This work successfully reports extraction and separation of hexavalent chromium from its model contaminant using a bulk liquid membrane ensemble. Aqueous NaOH solution was found to be the preferred stripping phase and *tri-n-octylamine* as the suitable carrier. The extraction-separation performance of the BLM module *via* different interphases was seen to be substantially influenced by the factors like: type of carrier and its concentration, nature of stripping phase, feed and stripping phase concentrations, pH of the feed phase etc. A key objective of this work was to achieve maximum separation of Cr (VI) with minimal carrier concentration and this work successfully reports a removal percentage of *ca*. 98% of Cr (VI) ions with 0.25 vol. % of TOA within a span of 2 hrs. The transport mechanism was observed to be more effective in the acidic pH range *w.r.t* the feed phase (*ca*. pH 1) whereas the optimum stripping phase concentration of NaOH was found to be *ca*. 0.3 N. Membrane reproducibility study showed that the performance of the liquid membrane remained largely unaffected even after fourfold use, showing promise in waste water related separation applications.

This work has many future ramifications. The scopes are highlighted below:

(a) For the same set of inventory, Cr (VI) separation can be studied in supported and emulsion liquid membrane ensembles and the relative performances can be compared.

(b) Environmentally more benign carriers and solvents can be selected from natural sources and their performances can well be studied.

(c) Other heavy metals like As, Cd, Hg, Pb can be studied in this BLM module.

(d) Importantly, the used chemicals from the set of experiments (as carefully stored) may well be used with building materials or other alternatives for their effective disposal and developing a product or process in achieving so.

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APPENDIX A

Table A.1: Table for Figure 4.1(a) – Selection of carrier (Feed Phase)

Time(min)	TOA	DOA	Aliquat-336	ITOA
0	100.00	100.00	100.00	100
15	48.46	54.53	39.58	36.76
30	20.42	36.09	22.10	22.27
45	12.51	32.13	10.07	23.84
60	7.58	12.86	3.31	15.76
75	5.46	7.17	0.68	7.88
90	3.78	4.67	0.98	5.47
105	3.84	3.73	0.64	3.34
120	3.66	3.45	1.73	3.06

Table A.2: Table for Figure 4.1(c) – Selection of carrier (Strip Phase)

Time(min)	TOA	DOA	Aliquat-336	ITOA
0	0	0	0	0
15	7.15	5.10	7.79	7.026
30	27.85	19.17	24.49	25.87
45	38.13	31.09	34.78	37.87
60	59.23	35.16	45.46	53.79
75	59.57	47.02	48.35	58.76
90	71.27	59.04	48.24	69.29
105	73.84	66.16	48.63	74.97
120	89.96	67.67	51.42	87.01

Table A.3: Table for Figure 4.2(a) – Effect of carrier concentration (Feed Phase)

Time (min)	0.1 Vol%	0.25 Vol%	0.5 Vol%	1 Vol%	2 Vol%	3 Vol%
0	100.00	100.00	100.00	100.00	100.00	100.00
15	72.22	53.02	48.60	48.46	37.40	35.43
30	43.36	26.18	22.19	20.42	20.17	17.07
45	32.74	26.77	17.75	12.51	13.14	14.67
60	29.02	18.47	17.72	7.58	8.26	5.01
75	23.03	11.02	7.24	5.46	6.52	2.05
90	16.02	6.71	7.75	3.78	4.09	1.10
105	12.39	5.52	9.098	3.84	3.37	0.72
120	6.96	4.79	6.28	3.66	8.35	0.57
135	5.72	5.28	4.12	3.65	4.17	0.78

Table A.4: Table for Figure 4.2(b) - Effect of carrier concentration (Strip Phase)

Time (min)	0.1 Vol%	0.25 Vol%	0.5 Vol%	1 Vol%	2 Vol%	3 Vol%
0	0	0	0	0	0	0
15	7.28	9.61	8.03	7.156	7.34	16.31
30	22.88	20.04	28.04	27.85	24.91	26.12
45	28.47	28.65	35.55	38.13	41.33	33.97
60	40.15	39.88	43.58	59.23	51.51	49.16
75	51.61	50.92	55.62	59.57	60.99	58.11
90	59.23	62.98	65.99	71.27	73.51	72.69
105	67.65	71.51	73.14	73.84	80.90	77.51
120	80.02	84.97	80.71	89.96	87.71	90.34

Table A.5: Table for Figure 4.3(a) -Different stripping phase

Time (min)	NaOH	KNO_3	Na_2CO_3	NaCl	Na_2SO_4
0	100.00	100.00	100.00	100.00	100.00
15	53.03	45.83	40.58	42.97	44.87
30	26.18	37.31	33.60	24.25	32.25
45	26.77	22.05	14.57	21.81	25.81
60	18.48	20.80	25.06	19.14	23.14
75	11.02	14.03	17.47	8.21	22.21
90	6.71	8.69	6.19	5.69	25.69
105	5.53	11.94	7.15	8.57	18.57
120	4.80	6.04	9.94	8.75	15.75

Table A.6: Table for Figure 4.3(c) -Different stripping phase

Time (min)	NaOH	KNO_3	Na_2CO_3	NaCl	Na_2SO_4
0	0	0	0	0	0
15	9.61	14.62	12.21	3.71	7.29
30	20.04	20.20	20.10	10.33	2.68
45	28.65	23.95	26.84	16.34	4.58
60	39.88	29.97	36.17	23.68	4.23
75	50.92	31.92	47.25	30.03	3.01
90	62.98	41.66	44.50	26.76	2.10
105	71.51	45.06	47.36	26.68	1.69
120	84.97	53.58	52.94	28.86	2.10

Table A.7: Table for Figure 4.4 –Effect of stripping phase concentration

Time (min)	0.1N	0.2N	0.3N	0.4N	0.5N
0	0	0	0	0	0
15	9.61	18.54	37.50	24.89	11.55
30	20.04	37.07	64.68	47.03	38.38
45	28.65	61.17	77.98	66.27	41.88
60	39.88	70.77	81.58	81.58	63.29
75	50.92	78.26	87.11	82.79	89.32
90	62.98	82.35	96.95	85.51	88.18
105	71.51	84.45	96.97	85.80	89.49
120	84.97	87.37	97.42	86.36	91.24

Table A.8: Table for Figure 4.5 – Effect of feed phase pH

Time (min)	pH=1	pH=2	pH=3	pH=4
0	100.00	100.00	100.00	100.00
15	21.99	51.71	60.09	80.02
30	17.35	39.62	40.84	76.18
45	11.42	25.49	30.39	68.77
60	7.95	10.28	27.43	63.47
75	6.66	9.01	22.51	52.02
90	5.00	8.07	21.40	45.21
105	2.30	9.40	19.09	40.52
120	2.56	6.39	19.51	40.29

Table A.9: Table for Figure 4.6–Effect of feed concentration

Time (min)	400ppm	200ppm	100ppm	50ppm
0	100.00	100.00	100.00	100.00
15	59.61	41.99	30.91	25.63
30	44.72	17.35	9.46	16.90
45	28.82	11.42	5.00	19.39
60	13.30	7.95	16.24	19.39
75	6.71	6.66	12.84	10.13
90	1.27	7.50	9.79	5.60
105	1.81	7.30	9.36	7.62
120	1.910	7.56	2.86	4.35

Table A.10: Table for Figure 4.7(a) – Reuse of Membrane (Feed Phase)

Time (min)	1st Time	2nd Time	3rd Time	4th Time
0	100.00	100.00	100.00	100.00
15	53.02	60.07	58.20	54.93
30	26.18	29.23	31.30	27.78
45	26.77	17.06	10.63	26.92
60	18.47	12.49	13.27	16.13
75	11.02	6.73	6.55	1.45
90	6.78	6.26	5.80	4.76
105	5.52	3.90	6.58	2.94
120	4.79	1.45	4.70	2.60

Table A.11: Table for Figure 4.7(b) – Reuse of Membrane (Strip Phase)

Time (min)	1st Time	2nd Time	3rd Time	4th Time
0	0	0	0	0
15	9.61	9.69	10.87	8.11
30	20.04	26.23	26.71	18.32
45	28.65	36.28	32.45	33.08
60	39.88	49.41	45.06	46.41
75	50.92	62.39	55.84	61.75
90	62.98	68.90	67.49	73.89
105	71.51	80.01	85.19	83.19
120	84.97	89.08	91.09	89.93